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SOME TRACE GAS EMISSIONS FROM NORTH AMERICAN BIOMASS FIRES WITH AN ASSESSMENT OF REGIONAL AND GLOBAL FLUXES FROM BIOMASS BURNING

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Abstract. Emission factors for several trace gases were determined using airborne measurements from 13 biomass fires in North America. Emissions of methane (CH_4), nonmethane hydrocarbons (NMHC), hydrogen (H_2) and ammonia (NH_3) were found to be positively correlated with the ratio of carbon monoxide (CO) to carbon dioxide (CO_2) emission factors, both within each fire and between fires. This indicates that these four species are produced predominantly when combustion is inefficient. Methyl chloride (CH_3Cl) emission factors were positively correlated with the ratio of CO to CO_2 emission factors within the majority of the fires. However, a linear regression of the average CH_3Cl emission factor for each fire onto the average ratio of the CO to CO_2 emission factors produced a negative correlation coefficient. This indicates that the variance in CH_3Cl emissions between fires is not due to differences in overall combustion efficiency. (According to previous research, differences in fuel chlorine content are mainly responsible for the differences in emissions of CH_3Cl between fires.) The average NO_x emission factors for three biomass fires in southern California were found to be significantly higher than the average NO_x emission factors for the remaining 10 fires studied. It is suggested that this difference is due to an enhanced nitrogen content (possibly the result of pollutant deposition and in some cases nitrogen fixation) of the fuels consumed, and the consumption of large amounts of foliage during the three fires. The average NO_x/CO_2 molar ratio determined from this study (2.1×10^{-3}) is consistent with results from other airborne and laboratory studies of biomass burning emissions. However, the N_2O/CO_2 molar ratios resulting from this study are roughly a factor of 2 larger than N_2O/CO_2 molar ratios obtained from laboratory studies. It is hypothesized that the higher N_2O/CO_2 molar ratios presented here are primarily due to emissions of N_2O from the soil. Overall average emission factors derived from this study were used to estimate the fluxes of several trace gases from temperate and boreal biomass fires. In addition, a new method is outlined for estimating fluxes of CH_4, NMHC, H_2 and NH_3 from global biomass burning. The annual emissions of these four species from worldwide biomass burning are determined by this method to be 39, 17, 21 and 4.5 Tg yr^{-1}, respectively. Our results indicate that the worldwide emissions of CH_4, NMHC, H_2 and NH_3 from biomass burning represent 8%, 17%, 24% and 7%, respectively, of the total global emissions of these four species.

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Introduction

Biomass burning is recognized to be a significant source of several trace gases in the atmosphere [cf. Crutzen et al., 1979, 1985]. Some of the gases emitted from burning activities (e.g., carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)) affect global climate due to their role as "greenhouse gases." Atmospheric chemistry and photochemistry are also affected by trace gas emissions from biomass burning. Hydrogen (H_2), another species emitted from biomass fires, reacts in the stratosphere to form water. It has been postulated that the resulting increase in the reservoir of stratospheric water vapor could affect the formation of stratospheric OH (hydroxyl radical). This, in turn, could have an impact on the chemical and thermal balance of the stratosphere [Crutzen et al., 1979]. Methyl chloride (CH_3Cl) has been suggested as a tracer for pollution from biomass burning [Khalil et al., 1985]. CH_3Cl is also of great importance to the stratospheric ozone budget, due to its role as a significant contributor of stratospheric chlorine [Andreae, 1991]. On local and regional levels, interest in trace gas emissions from biomass burning has arisen primarily out of the need to develop more effective smoke management policies for prescribed fires. Gaseous emissions from biomass fires are also of concern due to the removal of vital nutrients (e.g., nitrogen, potassium, phosphorus and sulfur) from various ecosystems as a result of burning activities [cf. White et al., 1973; DeBano and Conrad, 1978; Crutzen and Andreae, 1990].

Several different types of studies have been undertaken in efforts to delineate the factors governing trace gas emissions from biomass fires and to quantify the amounts of various trace gases released to the atmosphere from biomass combustion. Laboratory studies involving the combustion of biomass samples have yielded important information on gaseous emissions as a function of combustion phase [e.g., Hao et al., 1991; Lobert et al., 1991]. The impact of fire dynamics on trace gas emissions has been studied through the analysis of ground-based measurements obtained from instruments mounted on towers or suspended in the smoke of prescribed fires [Ward and Hardy, 1989; Susott et al., 1991]. Finally, airborne studies of the smokes from biomass fires have been carried out in order to measure directly the concentrations of various chemical species emitted to the atmosphere from large biomass fires [cf. Evans et al., 1977; Stith et al., 1981; Andreae et al., 1988; Cofer et al., 1989].

Between 1986 and 1990, the Cloud and Aerosol Research group at the University of Washington undertook airborne studies of the smokes from 13 biomass fires in North America. A substantial trace gas data set was compiled during the course of these field projects. Analysis of some of the trace gas data for several of the fires had been carried out previously [e.g., Hegg et al., 1987, 1988, 1990; Radke et al., 1991]. The purpose of the present study was to systematically review the available chemical data for all of the fires studied during the 5-year period and to undertake a comprehensive analysis of the emissions of several gaseous carbon and nitrogen species, H_2 and CH_3Cl. An additional goal of this study was to develop a new method for estimating global emissions of certain chemical species from biomass burning, and apply it to estimate worldwide emissions of CH_4, nonmethane hydrocarbons (NMHC), H_2 and ammonia (NH_3) from biomass burning.

Fires Studied and Methods of Measurement

Listed in Table 1 are the locations, dates, areas burned, fire types and fuel types for the 13 biomass fires examined in this study. The fires can be categorized into three ecosystems: Mediterranean, temperate forest and boreal. The Mediterranean ecosystem is located in the southwest United States and is characterized by the presence of chaparral fuels. The Eagle, Lodi I and Lodi II prescribed fires took place in this ecosystem. The temperate forest ecosystem consists primarily of coniferous fuels (e.g., ponderosa pine, lodgepole pine, Douglas fir, western hemlock, true fir and associated species). The Myrtle/Fall Creek, Silver, Troy and Mabel Lake fires all occurred in this region. The Myrtle/Fall Creek and Silver fires were wildfires that primarily consumed standing timber. In contrast, the Troy and Mabel Lake fires were prescribed burns of residues left from the harvesting of timber. The boreal ecosystem, which encompasses Alaska and the majority of Canada, is characterized by the presence of both coniferous and hardwood fuels. The five fires in Ontario, Canada (Table 1), were prescribed, and were for the purpose either of site preparation following commercial timber harvesting or of converting areas of unmerchantable species to species with commercial value. The fire in Alaska (fire A121) was a wildfire in standing black spruce. The locations and ecosystem classifications of the fires in this study are shown in Figure 1.

Measurements of the trace gas species discussed in this paper were obtained aboard the University of Washington's Convair C-131A research aircraft. The Convair is a twin-engine, propeller-driven aircraft that is equipped to carry a large instrumentation payload plus a scientific crew of up to eight persons. A complete description of the work stations and intrumentation layout on the aircraft has been given by Hobbs et al. [1991].

In general, samples were taken in the ascending smoke column and stabilized smoke plume of the fires and also in the adjacent ambient air. Both smoke and ambient samples were obtained using a 1.5 m^3 polyethylene bag that was filled by ram air. A portion of the air was drawn out of this bag and passed into evacuated stainless steel canisters. Postflight analysis of these canister samples yielded concentrations of CO_2, CO, CH_4, NMHC, H_2, N_2O and CH_3Cl (see Table 2 for a listing of the techniques used to analyze the canister samples). The error associated with the canister analyses is variable, ranging from 0.3 to 10% depending on the species being measured (Table 2).

Air from the sampling bag was also processed through two types of filters: 37 mm Teflon filters and oxalic acid impregnated filters (preceded by Teflon filters). The exposed 37 mm filters were analyzed using gravimetry to determine particle mass concentrations and subsequently the mass concentration of carbon in particles. Analysis of the oxalic acid/Teflon filters yielded the concentration of gaseous NH_3 in the samples (Table 2). The error in the NH_3 concentrations ranges from 5 to 60%, depending on the filter loading.

In addition to "grab" samples, continuous measurements of CO_2 and NO_x (nitric oxide plus nitrogen dioxide, $NO+NO_2$) concentrations were made on board the aircraft (see Table 2). The CO_2 instrument, a correlation spectrometer, was typically zeroed (using pure nitrogen (N_2)) and spanned (using a gas of known CO_2 concentration) at least once during each flight. The correlation spectrometer can measure from 0 to 1000 ppm CO_2 and has an error of ~4 ppm. The NO_x instrument, which was calibrated in the laboratory against a permeation tube and span gas dilution system, has a range of 0 to 5 ppm and an associated error of ~1 ppb.

Measurements of particle mass concentrations were made using a quartz microbalance impactor (Table 2) that was fed from a 90 L batch sample of air. This instrument measures

TABLE 1. Biomass Fires Examined in This Study

Fire	Location	Date	Area Burned, ha	Type	Fuel
Eagle	Ramona, California	Dec. 3, 1986	30	prescribed	black sage, sumac, chamise
Lodi I	Los Angeles, California	Dec. 12, 1986	40	prescribed	chaparral, chamise
Lodi II	Los Angeles, California	June 22, 1987	150	prescribed	chaparral, chamise
Hardiman	Chapleau, Ontario	Aug. 28, 1987	325	prescribed	jack pine, aspen, paper birch
Myrtle/Fall Creek	Roseburg, Oregon	Sept. 2, 1987	2,000	wildfire	pine, brush, Douglas fir
Silver	Grants Pass, Oregon	Sept. 17–19, 1987	20,000	wildfire	Douglas fir, true fir, hemlock
Troy	Troy, Montana	Oct. 8, 1987	70	prescribed	pine, Douglas fir, true fir
Battersby	Timmins, Ontario	Aug. 12, 1988	718	prescribed	jack pine, white and black spruce
Peterlong	Timmins, Ontario	Aug. 22, 1988	217	prescribed	jack pine, white and black spruce
Hill	Chapleau, Ontario	Aug. 10, 1989	486	prescribed	paper birch and poplar
Wicksteed	Hornepayne, Ontario	Aug. 12, 1989	700	prescribed	birch, poplar, mixed hardwoods
Mabel Lake	Kelowna, British Columbia	Sept. 25, 1989	29	prescribed	hemlock, deciduous, Douglas fir
Alaska (A121)	Fairbanks, Alaska	June 27–28, 1990	4,000*	wildfire	black spruce

*As of June 28, 1990.

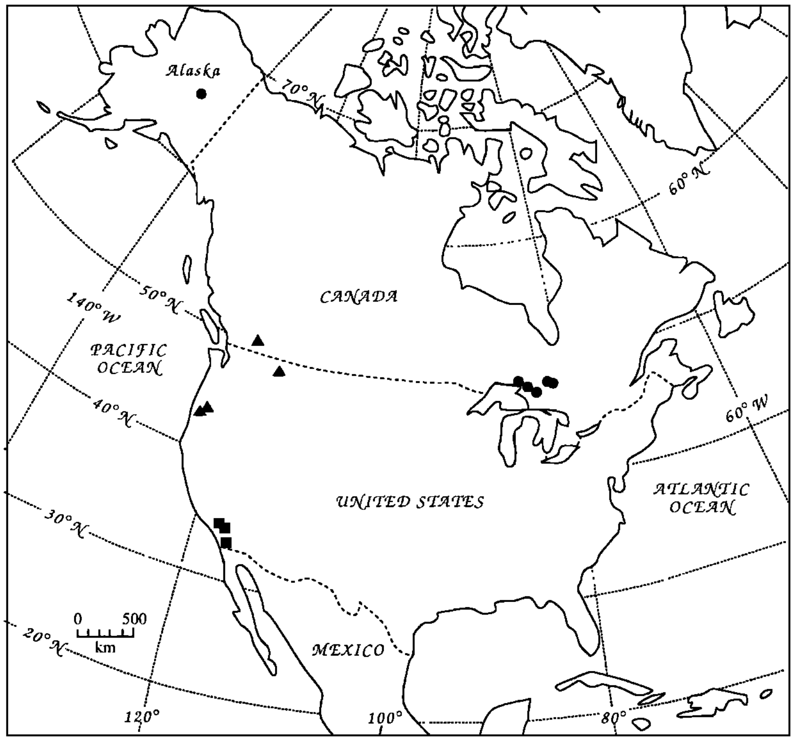

Fig. 1. Map showing the locations and ecosystem types of the 13 biomass fires examined in this study. Squares denote fires in the Mediterranean ecosystem, triangles fires in the temperate forest ecosystem, and circles fires in the boreal ecosystem.

mass concentration values ranging from 0.1 to 3000 $\mu g\ m^{-3}$ with an error of <0.2 $\mu g\ m^{-3}$. Aerosol data from the quartz microbalance impactor and aerosol mass concentrations from the 37 mm filters were used to determine the mass concentrations of carbon in particles.

Results

Emission Factors

Emission factors, defined as the mass of species emitted into the air per unit mass of fuel burned, were calculated using the carbon balance method [Ward et al., 1979; Nelson, 1982] as adapted for airborne sampling by Radke et al. [1988]. This method requires measurements of all major carbon-containing combustion products in the smoke plume. For this study, we considered the contributions of carbon from CO and CO_2 (the dominant sources of in-plume carbon), a subset of hydrocarbons (CH_4, C_2H_6, C_2H_2, C_3H_8, C_3H_6, i-C_4 and n-C_4) and particles. The mass of fuel needed to produce the emissions in a unit volume of air in the plume is equal to the ratio of the mass concentration of carbon in the plume to the mass fraction of carbon in the fuel. This ratio, when divided into the mass concentration of a particular combustion product X, gives the emission factor [EF(X)] of X in g kg^{-1}:

$$EF(X) = \frac{C_M(X)M_f}{C_P + C_{CO} + C_{CO_2} + C_{CH_4} + C_{NMHC}} \qquad (1)$$

where $C_M(X)$ is the excess (i.e., above-ambient) mass concentration of X in the plume (in $\mu g\ m^{-3}$) and C_P, C_{CO}, C_{CO_2}, C_{CH_4} and C_{NMHC} the excess mass concentrations (in $\mu g\ C\ m^{-3}$) of carbon from particles, CO, CO_2, CH_4 and NMHC, respectively. In this study, NMHC is taken to be the sum of ethane (C_2H_6), acetylene (C_2H_2), propane (C_3H_8), propene (C_3H_6), isobutane (i-C_4) and n-butane (n-C_4). M_f is the mass fraction of carbon in the fuel and has units of g kg^{-1}.

For this study, we assumed the mass concentration of carbon in particles to be 50% of the total particle mass. This estimate is based on results from studies of particulate emissions from forest fires and wood-burning fireplaces [Dasch, 1982; Patterson and McMahon, 1984; Ward and Hardy, 1988]. In an attempt to represent fuel diversity in the emission factor calculations, we used different values for M_f for each of the fires studied. M_f values for individual fires were estimated using values from the literature [Byram, 1959; Bollen, 1974; Susott et al., 1991]. The fuel carbon fraction values used in this study were all on the order of 0.5 x 10^3 g kg^{-1}: the minimum value used in the emission factor calculations was 0.497 x 10^3 g kg^{-1} (for the three fires in southern California) and the maximum 0.541 x 10^3 g kg^{-1} (for the wildfire in Alaska).

Listed in Table 3 are the average emission factors, with standard deviations, for several gaseous carbon species for the 13 biomass fires. Table 4 lists the average emission factors, and standard deviations, for H_2, CH_3Cl, N_2O, NO_x and NH_3 determined for these fires. Also given in Tables 3 and 4 are the overall average emission factors, with uncertainties, for the various chemical species. The uncertainty values listed in both tables are the total variance (i.e., the sum of the internal and external variance) of the emission factor data. Inspection of Tables 3 and 4 shows that the standard deviations for the individual fires are quite large, and are often equal to or greater than the associated average values. The errors associated with the measurements of the various combustion products are in general quite small. (The largest possible analytical errors, ± 50% and ± 60%, correspond to the measurement of particle

TABLE 2. Measurement Types and Analytical Techniques for Parameters in This Study

Parameter	Measurement Type*	Analytical Technique**	Analytical Error
CO_2	C,G	correlation spectrometer (C); GC/FID and GC/TCD (G)	±4 ppm; ±0.5% (GC/FID) and ±1% (GC/TCD)
CO	G	GC/FID	±5%
CH_4	G	GC/FID	±0.3 – 0.4%
NMHC	G	GC/FID	±10%
H_2	G	GC/RGD	±1%
NO_x	C	chemiluminescence (O_3)	±1 ppb
N_2O	G	electron capture gas chromatography	<±1%
NH_3	G	oxalic acid impregnated filter preceded by Teflon filter	±5 – 60%
CH_3Cl	G	electron capture gas chromatography	±3%
particle mass concentration	G	37 mm Teflon filter; quartz microbalance impactor	~±3 – 50% (filter values); <0.2 μg m^{-3} (impactor values)

*C is continuous measurement; G is "grab" sample.
**GC/FID is gas chromatograph and flame ionization detector; GC/TCD is gas chromatograph and thermal conductivity detector; GC/RGD is gas chromatograph and reduction gas detector.
References for some of the analytical techniques are as follows: GC/FID, Rasmussen and Khalil [1981]; GC/RGD, Khalil and Rasmussen [1990]; electron capture gas chromatography, Rasmussen et al. [1980]; and oxalic acid filter analysis, Hegg et al. [1988].

mass concentration and gaseous NH_3, respectively; see Table 2.) Consequently, measurement (i.e., instrumental) error is responsible for only a small portion of the uncertainty in the emission factors for the fires. The large variance in emissions within each fire (i.e., the intrafire variability) is therefore real and is mainly attributable to fire dynamics. Interfire variability, or the variance in emissions between the different fires, is governed primarily by the characteristics of the fuels (e.g., elemental composition, moisture content, size of components) [Ward, 1990].

Effect of Combustion Efficiency on Trace Gas Emissions

Biomass burning proceeds through two distinct combustion phases: flaming and smoldering. These phases differ both in appearance and in the types of trace gases emitted to the atmosphere [Ward, 1990]. During the flaming phase, large amounts of CO_2 (a product of complete combustion) are emitted, and combustion is referred to as being efficient. The emission of products of incomplete combustion (such as CO and hydrocarbons) increases during the smoldering phase, and combustion is said to be inefficient.

It is difficult to classify the trace gas emissions according to phase of combustion for the fires studied here. This is because in almost all cases fire behavior was very complex, so that quite often flaming and smoldering processes occurred simultaneously as large areas of fuel were burned. Nevertheless, it is possible to study the effect of combustion efficiency on trace gas emissions by examining the relationships between the emission factors for various chemical species and the ratio of the CO to CO_2 emission factors for each of the fires. The ratio of the CO to CO_2 emission factors is an indicator of the inefficiency of combustion. When combustion is inefficient, the CO/CO_2 emission factor ratio will have a high value. Conversely, when combustion is efficient this ratio has a low value.

To examine the effect of combustion efficiency on the variability of emissions within biomass fires, linear regressions of the emission factors for various chemical species onto the ratios of the CO to CO_2 emission factors were calculated for each of the 13 fires. Table 5 lists the correlation coefficients (r) that were obtained from these regression analyses.

For each fire, the CH_4 emission factors were positively correlated with the CO/CO_2 emission factor ratios (Table 5), and in most cases r was greater than 0.9. Emission factors for the individual nonmethane hydrocarbon species were, in general, positively correlated with the ratio of CO to CO_2

TABLE 3. Average Emission Factors (and Standard Deviations) for Several Gaseous Carbon Species From Thirteen Biomass Fires in North America

Fire	CO	CO_2	CH_4	C_2H_6	C_2H_2	C_3H_8	C_3H_6	i-C_4	n-C_4	NMHC*
Eagle	44 ± 23	1737 ± 45	1.0 ± 0.6	0.19 ± 0.11	0.11 ± 0.06	0.08 ± 0.06	0.30 ± 0.17	0.006 ± 0.005	0.011 ± 0.010	0.71 ± 0.39
Lodi I	76 ± 18	1667 ± 41	2.4 ± 1.2	0.37 ± 0.14	0.32 ± 0.06	0.22 ± 0.13	0.61 ± 0.23	0.064 ± 0.053	0.13 ± 0.10	1.72 ± 0.58
Lodi II	72 ± 20	1687 ± 36	3.3 ± 1.5	0.53 ± 0.19	0.22 ± 0.06	0.29 ± 0.15	0.45 ± 0.12	0.088 ± 0.130	0.093 ± 0.061	1.67 ± 0.55
Hardiman	74 ± 36	1794 ± 83	1.6 ± 1.3	0.39 ± 0.23	0.18 ± 0.07	0.17 ± 0.11	0.52 ± 0.28	0.026 ± 0.046	0.067 ± 0.098	1.36 ± 0.74
Myrtle/ Fall Creek	112 ± 21	1714 ± 39	3.3 ± 0.8	0.59 ± 0.11	0.22 ± 0.02	0.25 ± 0.05	0.74 ± 0.13	0.019 ± 0.003	0.050 ± 0.013	1.87 ± 0.32
Silver	96 ± 55	1695 ± 112	2.6 ± 1.5	0.59 ± 0.39	0.24 ± 0.13	0.34 ± 0.18	0.13 ± 0.16	0.088 ± 0.103	0.17 ± 0.16	1.57 ± 0.71
Troy	120 ± 66	1668 ± 173	4.3 ± 1.9	0.88 ± 0.47	0.30 ± 0.16	0.28 ± 0.13	1.00 ± 0.60	0.010 ± 0.008	0.038 ± 0.027	2.51 ± 1.24
Battersby	101 ± 85	1756 ± 156	3.7 ± 3.4	0.43 ± 0.48	0.23 ± 0.18	0.20 ± 0.16	0.62 ± 0.54	0.016 ± 0.014	0.055 ± 0.045	1.55 ± 1.38
Peterlong	131 ± 199	1668 ± 463	7.7 ± 10.1	0.94 ± 1.45	0.34 ± 0.52	0.35 ± 0.53	0.92 ± 1.31	0.020 ± 0.030	0.088 ± 0.136	2.65 ± 3.98
Hill	158 ± 125	1645 ± 252	8.9 ± 8.7	0.89 ±0.76	0.41 ± 0.29	0.15 ± 0.05	1.13 ± 0.87	0.023 ± 0.016	0.067 ± 0.050	2.67 ± 1.98
Wicksteed	79 ± 48	1792 ± 95	4.5 ± 3.2	0.61 ± 0.39	0.26 ± 0.14	0.20 ± 0.13	0.73 ± 0.47	0.015 ± 0.010	0.052 ± 0.038	1.87 ± 1.16
Mabel Lake	77 ± 34	1744 ± 65	3.2 ± 1.8	0.35 ± 0.19	0.20 ±0.05	0.10 ± 0.06	0.42 ± 0.19	0.007 ± 0.003	0.026 ± 0.010	1.11 ± 0.52
Alaska (A121)	89 ± 13	1788 ± 23	2.9 ± 1.1	0.72 ± 0.39	0.28 ± 0.07	0.25 ± 0.18	0.56 ± 0.20	0.010 ± 0.017	0.060 ± 0.078	1.89 ± 0.87
Overall average	95 ± 16	1720 ± 29	3.8 ± 1.0	0.58 ± 0.12	0.25 ± 0.04	0.22 ± 0.05	0.63 ± 0.14	0.030 ± 0.010	0.070 ± 0.018	1.78 ± 0.33

With the exception of the CO_2 emission factors for the Alaska fire, which were derived from continuous measurements of the CO_2 concentrations in the plume, the emission factors for the trace gases were derived from the analysis of "grab" samples of smoke collected in stainless steel canisters. Units are g kg^{-1}.

* NMHC emission factors for each fire were determined by summing the emission factors for C_2H_6, C_2H_2, C_3H_8, C_3H_6, i-C_4 and n-C_4.

TABLE 4. Average Emission Factors (and Standard Deviations) for H_2, CH_3Cl, N_2O, NO_x and NH_3 from Thirteen Biomass Fires in North America

Fire	H_2	CH_3Cl	N_2O	NO_x*	NH_3
Eagle	0.85 ± 0.47	0.032 ± 0.017	0.15 ± 0.05	14.5 ± 3.8	–
Lodi I	1.6 ± 0.5	0.032 ± 0.006	0.30 ± 0.15	8.5 ± 3.3	–
Lodi II	1.7 ± 0.6	0.041 ± 0.009	0.35 ± 0.35	4.2 ± 4.3	0.06 ± 0.08
Hardiman	0.94 ± 0.57	0.013 ± 0.007	0.47 ± 0.53	2.6 ± 2.1	0.26 ± 0.30
Myrtle/ Fall Creek	2.1 ± 0.5	–	0.18 ± 0.13	2.3 ± 0.4	0.70 ± 0.46
Silver	1.3 ± 0.9	0.012 ± 0.012	0.27 ± 0.44	0.92 ± 0.68	0.13 ± 0.14
Troy	3.3 ± 2.3	0.015 ± 0.012	1.3 ± 3.4	1.8 ± 0.8	0.57 ± 0.28
Battersby	1.6 ± 1.4	0.012 ± 0.009	–	2.5 ± 1.9	0.37 ± 0.21
Peterlong	4.2 ± 4.9	0.021 ± 0.033	–	2.7 ± 2.5	0.94 ± 0.55
Hill	3.1 ± 2.4	0.017 ± 0.011	0.39 ± 0.38	0.30 ± 0.33	–
Wicksteed	2.1 ± 1.4	0.013 ± 0.007	0.24 ± 0.15	0.37 ± 0.31	–
Mabel Lake	1.2 ± 0.6	–	0.032 ± 0.043	–	0.45 ± 0.30
Alaska (A121)	3.5 ± 5.6	0.043 ± 0.045	0.15 ± 0.09	1.6 ± 0.2	0.69 ± 0.33
Overall average	2.1 ± 0.5	0.023 ± 0.006	0.35 ± 0.13	3.5 ± 1.3	0.46 ± 0.16

Measurements of H_2, CH_3Cl and N_2O were obtained from the analysis of "grab" samples of smoke collected in stainless steel canisters. NO_x and NH_3 concentrations were obtained from continuous measurements and the analysis of filter samples, respectively. Units of emission factors are g kg^{-1}.
*NO_x = NO + NO_2. Of the NO_x, approximately 70 to 90% is NO_2.

emission factors: as is evident from Table 5, correlation coefficients for the various species were typically greater than 0.9. However, for some of the fires, linear regressions yielded $r < 0.5$, and, in a few cases, negative r values were obtained. The NMHC emission factors (defined as the sum of the emission factors for the six nonmethane hydrocarbon species) were in each case positively correlated with the CO/CO_2 emission factor ratios. With the exception of the Alaska wildfire, for which $r = 0.66$, the NMHC correlation coefficients were all greater than 0.8 (Table 5).

The regression results for CH_4, the individual nonmethane hydrocarbons and NMHC indicate that these species are produced predominantly when combustion is inefficient. Similar results have been obtained from laboratory studies involving the combustion of biomass samples [Lobert et al., 1991].

The H_2 emission factors were, for each of the 13 fires, positively correlated with the ratio of CO to CO_2 emission factors. As is indicated in Table 5, the correlation coefficients were, in general, greater than 0.9. (The one exception was the Alaska wildfire, for which $r = 0.47$.) These strong positive correlations are as expected based on the fact that H_2 is a product of incomplete combustion.

Regression analyses involving CH_3Cl emission factors and the ratio of CO to CO_2 emission factors also yielded significant results. With the exception of the Silver and Alaska fires (for which the r values were 0.17 and 0.11, respectively), the r values were all greater than ~0.9 (Table 5). For seven of the fires, r was greater than or equal to 0.95. Thus, our results indicate that CH_3Cl is emitted from biomass fires primarily when combustion is inefficient. Reinhardt [1987] arrived at a similar conclusion from a laboratory study of chlorinated emissions from forest fuel combustion.

Linear regressions of the NH_3 emission factors onto the CO/CO_2 emission factor ratios were performed for eight of the fires for which NH_3 data were available. (Only two NH_3 emission factors were calculated for the Hardiman fire; hence, a linear regression of the NH_3 emission factors onto the ratio of CO to CO_2 emission factors could not be calculated.) For six of the fires, the NH_3 emission factors were positively correlated with the ratios of CO to CO_2 emission factors (see Table 5). (The exceptions were the Troy and Battersby fires, for which the r values were –0.075 and –0.09, respectively.) Furthermore, for five of those six fires (Myrtle/Fall Creek, Silver, Peterlong, Mabel Lake and Alaska) r was ≥ 0.8. These results suggest that NH_3 is emitted from biomass fires primarily when combustion is inefficient. Lobert et al. [1991] obtained similar results in laboratory studies of nitrogenous emissions from biomass burning.

The positive correlation between NH_3 emission factors and the ratio of CO to CO_2 emission factors is a direct consequence of the process whereby nitrogen compounds are emitted and subsequently oxidized during combustion. When heated, fuel-bound nitrogen compounds undergo thermal decomposition, and low molecular weight compounds such as NH_3 are emitted [Glassman, 1977]. If the supply of oxygen is good, NH_3 is rapidly oxidized to NO and other oxides of nitrogen. However, as combustion becomes increasingly inefficient, less of the NH_3 undergoes oxidation and emissions of NH_3 increase.

Laboratory experiments have been undertaken to study how emissions of NO_x and N_2O from biomass burning are related to the phase of combustion. Lobert et al. [1991] and Hao et al. [1991] found that the emissions of both species are highest during the flaming phase, when combustion is efficient. Based on these results, we hypothesized that the NO_x and N_2O emission factors determined for each of the fires in this study would be anticorrelated with the ratios of CO to CO_2 emission factors. However, linear regression calculations involving the NO_x and N_2O emission factors and the CO/CO_2 emission factor ratios yielded ambiguous results: while in some cases the NO_x and N_2O emission factors were

TABLE 5. Correlation Coefficients (r) From Linear Regressions of Emission Factors for Various Trace Gases Onto the Ratio of CO to CO_2 Emission Factors

Fire	CH_4	C_2H_6	C_2H_2	C_3H_8	C_3H_6	i-C_4	n-C_4	NMHC*	H_2	CH_3Cl	N_2O	NO_x	NH_3
Eagle	0.98	0.99	0.96	0.94	0.96	0.78	0.75	0.98	0.998	0.98	0.27	–0.60	–
Lodi I	0.59	0.96	0.60	0.93	0.32	0.94	0.90	0.88	0.97	0.87	–0.34	0.45	–
Lodi II	0.997	0.95	0.79	0.94	0.93	0.063	0.89	0.96	0.96	0.87	–0.05	–0.86	0.42
Hardiman	0.95	0.99	0.97	0.98	0.99	0.24	0.21	0.97	0.99	0.97	–0.15	0.21	–
Myrtle/ Fall Creek	0.95	0.95	0.97	0.93	0.96	0.93	0.99	0.97	0.98	–	–0.29	–0.20	0.97
Silver	0.47	0.99	0.90	0.69	–0.056	–0.10	–0.091	0.83	0.91	0.17	0.24	0.18	0.87
Troy	0.65	0.96	0.99	–0.084	0.99	–0.28	–0.30	0.96	0.999	0.99	0.93	0.22	–0.075
Battersby	0.998	0.88	0.98	0.99	0.999	0.99	0.96	0.99	0.997	0.995	–	–0.11	–0.09
Peterlong	0.95	0.97	0.99	0.98	0.96	0.96	0.98	0.97	0.98	0.995	–	0.96	0.88
Hill	0.998	0.99	0.997	–0.003	0.996	0.98	0.99	0.99	0.996	0.98	0.97	–	–
Wicksteed	0.999	0.99	0.95	0.99	0.999	0.96	0.94	0.999	0.98	0.95	0.44	–0.91	–
Mabel Lake	0.997	0.99	0.99	0.99	0.99	0.98	0.96	0.99	0.99	–	–0.46	–	0.96
Alaska (A121)	0.34	0.66	0.45	0.62	0.64	0.38	0.51	0.66	0.47	0.11	0.33	0.40	0.80

* NMHC = C_2H_6 + C_2H_2 + C_3H_8 + C_3H_6 + i-C_4 + n-C_4.

anticorrelated with the CO/CO_2 emission factor ratios, in several instances either one or both of the nitrogen species were positively correlated with the CO/CO_2 emission factor ratios (see Table 5). The lack of a clear anticorrelation between the NO_x and N_2O emission factors and the CO/CO_2 emission factor ratios illustrates the fact that other variables, in addition to the efficiency of combustion, affect the emission of NO_x and N_2O from biomass fires. In particular, the amounts of NO_x and N_2O produced from biomass combustion are known to be dependent on, and to increase with, the nitrogen content of the fuel [Clements and McMahon, 1980; Hao et al., 1991; Lobert et al., 1991].

Regression analyses were also used to study the effect of combustion efficiency on emissions variance between biomass fires. Linear regressions of the average CH_4, NMHC, H_2 and NH_3 emission factors onto the average ratio of CO to CO_2 emission factors were calculated. These four regressions are shown in Figures 2, 3, 4 and 5.

The regression analysis using the average CH_4 emission factors given in Table 3 yielded $r = 0.87$ significant at >99% confidence level (Figure 2). The average NMHC emission factors from Table 3 were also positively correlated with the average ratios of the CO to CO_2 emission factors: the regression analysis yielded $r = 0.82$ significant at >99% confidence level (Figure 3). The regression analysis involving the average H_2 emission factors from Table 4 and the average CO/CO_2 emission factor ratios yielded $r = 0.78$, significant at >99% confidence level (Figure 4). The linear regression of the average NH_3 emission factors from Table 4 onto the average CO/CO_2 emission factor ratios gave $r = 0.70$, significant at >95% confidence level (Figure 5).

An interesting result was obtained from a linear regression of the average CH_3Cl emission factors (Table 4) onto the average ratio of CO to CO_2 emission factors. Instead of producing a positive correlation, this calculation yielded $r = -0.28$. This indicates that the variance in CH_3Cl emissions between the fires was not due to differences in overall combustion efficiency. Reinhardt [1987] determined that the

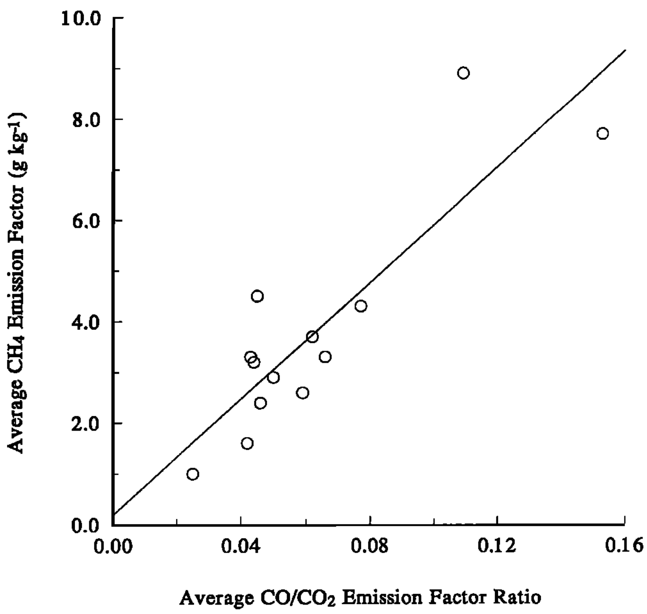

Fig. 2. Linear regression of the average CH_4 emission factor onto the average CO/CO_2 emission factor ratio for the fires in this study. Correlation coefficient (r) = 0.87.

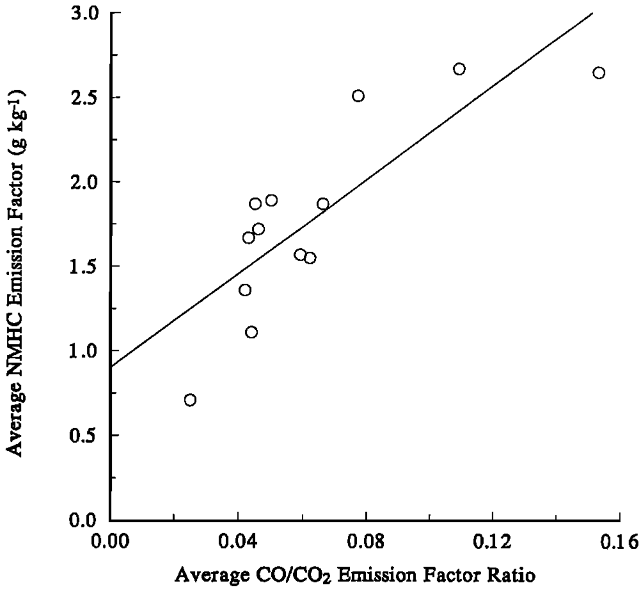

Fig. 3. Linear regression of the average nonmethane hydrocarbon (NMHC) emission factor onto the average CO/CO_2 emission factor ratio for the fires in this study. Correlation coefficient (r) = 0.82.

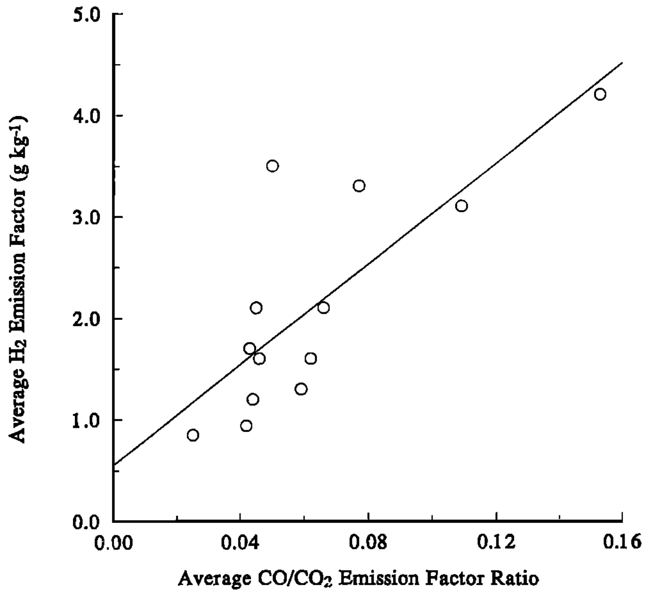

Fig. 4. Linear regression of the average H_2 emission factor onto the average CO/CO_2 emission factor ratio for the fires in this study. Correlation coefficient (r) = 0.78.

dominant factor governing the total amount of CH_3Cl emitted from a biomass fire is the chlorine content of the biomass. Based on this finding, our regression results for CH_3Cl are not surprising.

As described below, the linear regression results for CH_4, NMHC, H_2 and NH_3 can be used to estimate the global emissions of these four species from biomass burning.

Emissions of NO_x From the Fires in Southern California

Inspection of Table 4 reveals that the average NO_x emission factors for the Eagle, Lodi I and Lodi II fires are

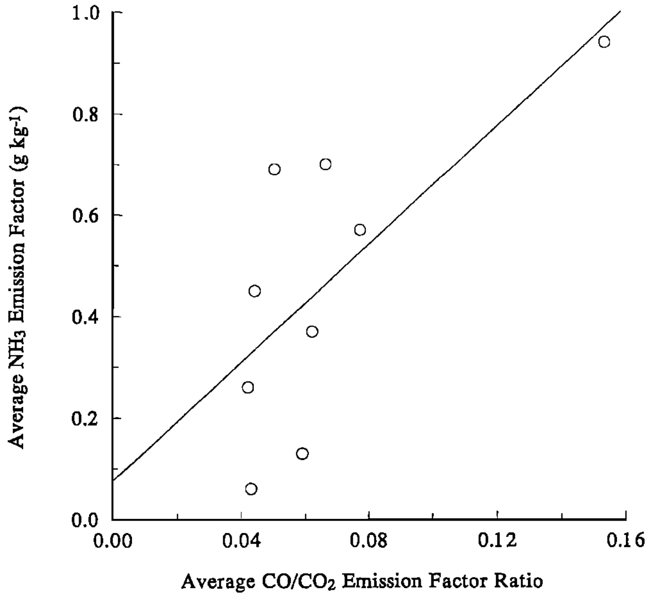

Fig. 5. Linear regression of the average NH_3 emission factor onto the average CO/CO_2 emission factor ratio for the fires in this study. Correlation coefficient (r) = 0.70.

significantly higher than the average NO_x emission factors for the remaining 10 biomass fires. While further research is needed to determine the exact cause of the high NO_x emissions from the southern California fires, we describe below two factors that could together contribute to the high NO_x emissions.

The first factor could be a high nitrogen content of the fuels consumed by the Eagle, Lodi I and Lodi II fires. Pollutant deposition may play a role in enhancing the nitrogen content of vegetation consumed by fires in southern California. Hegg et al. [1987] postulated that high emissions of NO_x from the Eagle and Lodi I fires were due to the revolatilization of pollutants deposited onto the fuel bed. Bytnerowicz et al. [1987] studied the dry deposition of acidic particles to chaparral foliage in the San Dimas Experimental Forest in southern California (the forest in which the Lodi I and Lodi II fires took place) and obtained a deposition flux for nitrate (NO_3^-) (3.60 μeq m^{-2} h^{-1}) that was substantially higher than NO_3^- deposition fluxes determined for a plant canopy in the eastern United States (0.08-0.27 μeq m^{-2} h^{-1}). These high levels of NO_3^- deposition are attributable to the high ambient concentrations of NO_x, NO_3^- and HNO_3 in the South Coast (Los Angeles) Air Basin [Bytnerowicz et al., 1987]. It is possible that some of the deposited NO_3^- interacts with the chaparral foliage and increases the nitrogen content of the biomass. Similar processes of deposition and plant assimilation could occur in the San Diego area, where the Eagle fire occurred. While ambient concentrations of NO_x in the San Diego Air Basin are generally not as high as those in the South Coast Air Basin [California Air Resources Board, 1986], high NO_x levels are nevertheless often recorded in the San Diego area. On the basis of these high NO_x concentrations, and the known ability of NO_x to interact with plants directly and after oxidation to HNO_3 and NO_3^- [Hosker and Lindberg, 1982], it seems likely that pollutant deposition could enhance the nitrogen content of biomass in the San Diego area.

Nitrogen fixation in the vegetation could also increase the nitrogen content of some of the fuels consumed by the fires in southern California. Ceanothus, the dominant type of chaparral consumed by the Lodi fires, can produce large root nodules in which N_2 fixation is active [Riggan et al., 1988]. Further research is needed to quantify the contribution of this nitrogen fixation to the nitrogen content of Ceanothus. However, it must be noted that nitrogen fixation does not explain the high average NO_x emission factor for the Eagle fire, which consumed black sage, sumac and chamise rather than Ceanothus.

The second factor contributing to the high NO_x emissions from the three southern California fires could be the nature of the fires. The Lodi I and Lodi II fires consumed primarily standing chaparral. Such fires have been observed to consume all of the foliage and deadwood and 9% of the live wood (P. J. Riggan, personal communication, 1991). The high NO_x emissions from the two Lodi fires could therefore be partly attributable to the fact that large amounts of foliage, which has a high nitrogen content, were consumed. Although exact information on the nature of the Eagle fire is not available, it seems plausible that significant quantities of foliage were consumed and that this could have contributed to the high NO_x emissions from the Eagle fire.

Comparison of the N_2O and NO_x Emissions With Results From Other Airborne and Laboratory Studies

Emissions of N_2O and NO_x from biomass fires are often expressed as molar ratios relative to CO_2 [e.g., Crutzen et al., 1985; Andreae et al., 1988; Cofer et al., 1989, 1991; Hao et al., 1991; Lobert et al., 1991]. To compare our results with those obtained in previous studies, we determined N_2O/CO_2 and NO_x/CO_2 molar ratios for the fires in this study using the average CO_2, N_2O and NO_x emission factors given in Tables 3 and 4. The results of these calculations, along with the average molar ratios, are presented in Table 6.

The average NO_x/CO_2 molar ratio from Table 6 ($2.1 \times 10^{-3} \pm 2.5 \times 10^{-3}$) is identical to the emission ratios determined by Crutzen et al. [1985] and Andreae et al. [1988] from airborne studies of biomass burning in Brazil. These authors reported NO_x/CO_2 ratios of $\sim 2 \times 10^{-3}$ and $\sim 2.1 \times 10^{-3}$, respectively. Our average NO_x/CO_2 molar ratio is also in agreement with the average molar ratio reported by Lobert et al. [1991] (2.0×10^{-3}) from laboratory studies of biomass burning.

The N_2O/CO_2 molar ratios from Table 6 are in very good agreement with the N_2O/CO_2 ratios reported by Cofer et al. [1989, 1991] from their studies of emissions from chaparral, boreal and wetlands fires. These authors obtained N_2O/CO_2 molar ratios ranging from $\sim 1 \times 10^{-4}$ to $\sim 4 \times 10^{-4}$.

However, the N_2O/CO_2 molar ratios determined from this study are roughly a factor of 2 larger than the N_2O/CO_2 ratios reported by Hao et al. [1991] and Lobert et al. [1991] from their laboratory studies of biomass burning emissions. It has been suggested that N_2O/CO_2 molar ratios obtained from airborne studies such as ours may be too high due to artifact production of N_2O in stainless steel canisters [Lobert et al., 1991; Hao et al., 1991]. No laboratory tests were done to determine if artifact production of N_2O affected the canister samples used in this study. Consequently, there is some uncertainty associated with the N_2O emissions data we present here, and the possibility of some artifact production of N_2O cannot be completely dismissed. However, we do not believe that artifact production accounts for all of the difference between our N_2O/CO_2 molar ratios and those obtained from laboratory studies. Muzio and Kramlich [1988] determined that the production of N_2O in stainless steel canisters is

TABLE 6. N_2O/CO_2 and NO_x/CO_2 Molar Ratios for the Biomass Fires in This Study

Fire	N_2O/CO_2	NO_x/CO_2
Eagle	8.6×10^{-5}	8.7×10^{-3}
Lodi I	1.8×10^{-4}	5.4×10^{-3}
Lodi II	2.1×10^{-4}	2.7×10^{-3}
Hardiman	2.6×10^{-4}	1.5×10^{-3}
Myrtle/Fall Creek	1.0×10^{-4}	1.3×10^{-3}
Silver	1.6×10^{-4}	5.4×10^{-4}
Troy	7.8×10^{-4}	1.1×10^{-3}
Battersby	–	1.5×10^{-3}
Peterlong	–	1.7×10^{-3}
Hill	2.4×10^{-4}	1.8×10^{-4}
Wicksteed	1.3×10^{-4}	2.1×10^{-4}
Mabel Lake	1.8×10^{-5}	–
Alaska (A121)	8.4×10^{-5}	8.9×10^{-4}
Average and standard deviation	$2.0 \times 10^{-4} \pm 2.0 \times 10^{-4}$	$2.1 \times 10^{-3} \pm 2.5 \times 10^{-3}$

The ratios were calculated using the average CO_2, N_2O and NO_x emission factors given in Tables 3 and 4.

dependent on the presence of SO_2, NO and moisture in the samples, with significant N_2O production occurring only if SO_2 concentrations in the samples are >600 ppm. Typical concentrations of SO_2 measured in the smoke plumes of fires in this study are ~1–15 ppb. We therefore believe that artifact production of N_2O is responsible for only a fraction of the discrepancy between our results and those obtained from laboratory studies.

In our opinion, the discrepancy between airborne and laboratory measurements of N_2O emissions could be due largely to an additional source of N_2O that is not accounted for in laboratory studies. More specifically, we believe that the heating of soil during biomass fires could lead to higher N_2O emissions. Gaseous N_2O collects in soils as a result of denitrification and nitrification by bacteria [Warneck, 1988]. It seems likely that the heating of soil during the combustion of biomass stimulates the release of significant quantities of N_2O. The existence of such a biogenic N_2O source has also been suggested by Cofer et al. [1991]. Laboratory studies typically involve the combustion of biomass samples alone; soil samples are generally not included. As a result, the contribution of soil heating to N_2O emissions would remain undetected. In the case of airborne studies of biomass combustion, both components (plant material and soil) are included and higher N_2O/CO_2 molar ratios would be expected.

Estimated Fluxes of Various Trace Gases From Temperate and Boreal Biomass Fires and Global Biomass Burning

The most straightforward method for determining the flux of a particular chemical species from biomass fires is to multiply the amount of biomass burned annually by the emission factor for that species. Using the overall average emission factors given in Tables 3 and 4 and an estimate of the amount of biomass burned annually in temperate and boreal forests (500 Tg yr^{-1} [Crutzen and Andreae, 1990]), we estimated the fluxes of several trace gases from temperate and boreal fires (see Table 7). (The amount of biomass burned annually in temperate and boreal forests is not well quantified, and the uncertainty associated with Crutzen and Andreae's estimate could be as great as a factor of 2. We believe the value of 500 Tg yr^{-1} to be the best estimate at present, and it was therefore used in this study.) In formulating these estimates we assumed that the emission factors derived from our measurements are representative of those for fires in all temperate and boreal areas. Given the locational diversity of the fires in this study (see Table 1 and Figure 1), this is a reasonable assumption.

TABLE 7. Flux Estimates for Several Trace Gases From Temperate and Boreal Biomass Fires

Species	Estimated Flux (Tg yr^{-1})
CO	48
CO_2	860
CH_4	1.9
NMHC	0.89
H_2	1.1
CH_3Cl	0.012
N_2O	0.18
NO_x	1.8
NH_3	0.23

Fluxes were calculated using the overall average emission factors for the various chemical species given in Tables 3 and 4 and an estimate of the amount of biomass burned annually in temperate and boreal forests (500 Tg yr^{-1} [Crutzen and Andreae, 1990]).

The flux estimates for CO, CO_2, CH_4 and NMHC listed in Table 7 are, in general, in fairly good agreement with those reported by Ward and Hao [1991]. These authors obtained a flux of CO from temperate and boreal fires that is identical to ours (48 Tg yr^{-1}). The CO_2 flux given in Table 7 (860 Tg yr^{-1}) is slightly higher than the value reported by Ward and Hao (770 Tg yr^{-1}). Conversely, the CH_4 flux we determined for temperate and boreal fires (1.9 Tg yr^{-1}) is somewhat lower than the flux obtained by Ward and Hao (3.1 Tg yr^{-1}). The annual emission of NMHC reported by Ward and Hao (2.2 Tg yr^{-1}) is roughly a factor of 2 larger than our estimated NMHC flux (0.89 Tg yr^{-1}). However, since we have considered only a subset of the nonmethane hydrocarbons in our calculations (see Table 3), this discrepancy is not surprising.

The estimated flux of N_2O from temperate and boreal biomass fires listed in Table 7 (0.18 Tg yr^{-1}) is significantly higher than the value reported by Hao et al. [1991] (0.028 Tg yr^{-1}), which was based on laboratory experiments. As discussed previously, we believe this discrepancy could be due, in part, to an additional biogenic source of N_2O that is not accounted for in laboratory studies.

Reliable estimates of global trace gas emissions from biomass burning are of critical importance for assessing the impact of biomass burning on global atmospheric chemistry and climate change. Initial emission estimates for biomass burning were obtained by multiplying emission ratios of various chemical species relative to CO_2 by an estimate of the amount of CO_2 emitted annually from biomass burning [cf. Crutzen et al., 1979, 1985; Andreae et al., 1988]. While these efforts provided important preliminary information on the magnitude of global emissions from biomass burning, further research has shown that a more dynamical approach to estimating worldwide fluxes must be employed: rather than assuming that gaseous emissions are the same for all biomass fires, it is necessary to consider the effects of fuel composition and fire dynamics on trace gas emissions in order to better estimate fluxes from biomass fires. Biomass burning occurs in a wide range of ecosystems worldwide, and the diversity of fuels consumed (combined with significant variations in fire behavior) results in markedly different gaseous emissions [Ward, 1990].

In this study we have shown that the average emission factors for CH_4, NMHC, H_2 and NH_3 are positively correlated with the average ratio of CO to CO_2 emission factors for the fires in this study. These correlation results can be used to estimate the global emissions of CH_4, NMHC, H_2 and NH_3 from biomass burning.

The regression equations, and the associated correlation coefficients (r), determined from the results shown in Figures 2 to 5 are as follows:

$$EF(CH_4) = 57.18(MR) + 0.19 \quad (r = 0.87) \quad (2)$$

$$EF(NMHC) = 13.93(MR) + 0.90 \quad (r = 0.82) \quad (3)$$

$$EF(H_2) = 24.72(MR) + 0.55 \quad (r = 0.78) \quad (4)$$

$$EF(NH_3) = 5.85(MR) + 0.08 \quad (r = 0.70) \quad (5)$$

where MR is the ratio of CO to CO_2 emission factors. (MR is hereafter referred to as the CO/CO_2 mass ratio.) If it is assumed that (2)–(5) apply not only to biomass fires in temperate and boreal ecosystems but also to fires in other ecosystems, it is possible to substitute values of MR for various combustion sources into (2)–(5) and derive values for the corresponding emission factors. This approach is based on the premise that variations in fuel characteristics and fire behavior will cause variations in combustion efficiency, and subsequently variations in the emission factors for CH_4, NMHC, H_2 and NH_3. The advantage of this approach is that it allows for variations in emissions between different types of fires. It may therefore yield more accurate estimates of emissions from biomass burning worldwide than previous methods, which have assumed constant emissions from all biomass fires [e.g., Crutzen et al., 1979, 1985; Andreae et al., 1988].

Using MR values obtained from the literature and equations (2)–(5) above, we calculated emission factors for CH_4, NMHC, H_2 and NH_3 for the combustion of tropical forest, savanna, fuel wood and agricultural waste. These four sources, together with the combustion of temperate and boreal forest, are the main contributors to global biomass burning emissions [Andreae, 1991]. Table 8 lists the CO/CO_2 mass ratio estimates, the associated references, and the derived emission factors.

The fluxes of CH_4, NMHC, H_2 and NH_3 from the combustion of biomass worldwide were calculated using the emission factors in Table 8 and estimates of the amounts of biomass burned annually. The flux values for temperate and boreal biomass fires were taken from Table 7. The values used for the amounts of biomass burned annually and the estimated fluxes from the five combustion sources are summarized in Table 9. Also given in Table 9 are total flux estimates for CH_4, NMHC, H_2 and NH_3. The exact amounts of biomass consumed each year by the combustion of temperate and boreal forest, tropical forest, savanna, fuel wood and agricultural waste are highly uncertain. The values used in this study are the best, most recent, estimates of the amounts of biomass burned annually.

We have not attempted to estimate the fluxes of CH_3Cl, N_2O and NO_x from global biomass burning. The work of other researchers [Reinhardt, 1987; Lobert et al., 1991; Hao et al., 1991] has shown that the amounts of CH_3Cl and of N_2O and NO_x emitted from a fire are dependent on the chlorine and nitrogen contents, respectively, of the fuel. Consequently, the fuel content, rather than the combustion efficiency, must be used as the independent variable in equations to predict global emissions of these chemical species. (Such an approach was used by Lobert et al. [1991] and Hao et al. [1991], who present regression equations in which the fuel nitrogen content is used as the independent variable to predict emissions of N_2O and NO_x.) The lack of information on the chlorine and nitrogen content of the fuels consumed by the fires in this study made it impossible for us to derive accurate equations relating the emissions of CH_3Cl, N_2O and NO_x to fuel content. We therefore limited our flux calculations for these three species to estimates for temperate and boreal biomass fires.

Our estimate of the total flux of CH_4 from global biomass burning (39 Tg yr^{-1}; see Table 9) is higher than the total flux value reported by Ward and Hao [1991] (28 Tg yr^{-1}). The estimated total flux of NMHC listed in Table 9 (17 Tg yr^{-1}) is only slightly lower than Ward and Hao's [1991] estimate of 21 Tg yr^{-1}.

It is interesting to note that Ward and Hao [1991] employed a method similar to ours to produce their estimates of global emissions from biomass burning. They used a quantity called the "modified combustion efficiency (MCE)" as the independent variable in regression equations to predict emission factors, and subsequently worldwide emissions, for CH_4 and NMHC. (The MCE is defined as the ratio of carbon in CO_2 to the sum of carbon in CO and CO_2.) The similarities between our total flux estimates for CH_4 and NMHC and those of Ward and Hao [1991] indicate that both methods offer

TABLE 8. CO/CO_2 Mass Ratio Estimates and Associated Emission Factors for Four Biomass Burning Sources

Source	CO/CO_2 Mass Ratio (Source*)	Emission Factor (g kg^{-1})			
		CH_4	NMHC	H_2	NH_3
Tropical forest	0.076 (G)	4.5	1.96	2.4	0.52
Savanna	0.071 (BG,G)	4.2	1.89	2.3	0.50
Fuel wood	0.115 (C)	6.8	2.50	3.4	0.75
Agricultural waste	0.050 (D,BL)	3.0	1.60	1.8	0.37

Emission factors for the four sources were determined using the CO/CO_2 mass ratio values listed and the regression equations for CH_4, NMHC, H_2 and NH_3 given in the text.
*G denotes Greenberg et al. [1984]. BG, Bonsang et al. [1991]. C, Crutzen et al. [1979]. D, Darley et al. [1966]. BL, Boubel et al. [1969].

TABLE 9. Amounts of Biomass Burned Annually and Estimated Fluxes of CH_4, NMHC, H_2 and NH_3 from Global Biomass Burning

Source	Amount of Biomass Burned Annually (Source*)	Estimated Flux (Tg yr^{-1})			
		CH_4	NMHC	H_2	NH_3
Tropical forest	1259 (H)	5.7	2.5	3.0	0.65
Savanna	3691 (H)	16	7.0	8.5	1.8
Temperate and boreal forest	500 (C)	1.9	0.89	1.1	0.23
Fuel wood	1430 (A)	9.7	3.6	4.9	1.1
Agricultural waste	2020 (A)	6.1	3.2	3.6	0.75
Total flux		39	17	21	4.5
Percentage of total global emission**		8	17	24	7

With the exception of the flux values for temperate and boreal forest, which are from Table 7, the flux values listed were derived from the amounts of biomass burned annually and the emission factors given in Table 8.
*H denotes Hao et al. [1990]. C, Crutzen and Andreae [1990]. A, Andreae [1991].
**Percentage values are based on the following estimates for worldwide fluxes from all sources: CH_4 – 500 Tg yr^{-1} [Cicerone and Oremland, 1988]. NMHC – 100 Tg yr^{-1} [Ehhalt et al., 1986]. H_2 – 89 Tg yr^{-1} [Warneck, 1988]. NH_3 – 66 Tg yr^{-1} [Warneck, 1988].

equally viable approaches to assessing global emissions of certain trace gases from biomass burning.

The total flux values for CH_4, H_2 and NH_3 listed in Table 9 (39, 21 and 4.5 Tg yr^{-1}, respectively) are similar to the total flux estimates for the same three species reported by Andreae [1991] (51, 19 and 6.4 Tg yr^{-1}, respectively). Andreae's value for the global flux of NMHC from biomass burning (24 Tg yr^{-1}) is somewhat higher than our estimated flux of 17 Tg

yr^{-1}. This discrepancy could be due, in part, to the fact that only a subset of all nonmethane hydrocarbons were included in our calculations (see Table 3), whereas Andreae's flux estimate for NMHC includes all of the C_2 to C_{10} nonmethane hydrocarbons.

The contribution of biomass burning to the global budgets of CH_4, NMHC, H_2 and NH_3 can readily be assessed by comparing the total flux estimates in Table 9 with the total emissions from all sources.

Cicerone and Oremland [1988] estimated the emission of CH_4 from all sources to be ~500 Tg yr^{-1}. The flux of CH_4 from global biomass burning (39 Tg yr^{-1}) is 8% of this value. The annual emission of NMHC from biomass fires (17 Tg yr^{-1}) contributes 17% of the global flux of NMHC from all sources (~100 Tg yr^{-1} [Ehhalt et al., 1986]). The total flux of H_2 from biomass burning worldwide represents 24% of total global emissions (~89 Tg yr^{-1} [Warneck, 1988]). The total source strength for NH_3 was estimated by Warneck [1988] to be ~66 Tg yr^{-1}. The flux of NH_3 from biomass burning (4.5 Tg yr^{-1}) contributes 7% to this total global emission.

Summary and Conclusions

The results presented in this paper show that CH_4, NMHC, H_2, CH_3Cl and NH_3 are emitted from biomass fires primarily when combustion is inefficient. Furthermore, the total amount of CH_4, NMHC, H_2 and NH_3 emitted from a fire depends on the overall combustion efficiency of the fire. However, our results also indicate that the total amount of CH_3Cl produced by biomass combustion is not dependent on overall combustion efficiency. According to previous research, the chlorine content of the fuel is the main factor governing how much CH_3Cl is emitted by a fire.

The average NO_x emission factors for three prescribed fires in southern California were found to be significantly higher than the average NO_x emission factors for the other 10 fires in this study. Although further study is needed, we believe that two factors could together contribute to these elevated emissions: an enhanced nitrogen content, possibly the result of pollutant deposition and in some cases nitrogen fixation, of the fuels consumed, and the consumption of large amounts of foliage during the three fires.

The average CO_2, N_2O and NO_x emission factors were used to determine N_2O/CO_2 and NO_x/CO_2 molar ratios for the 13 fires in this study. The average NO_x/CO_2 molar ratio derived from this study is in agreement with values obtained from other airborne and laboratory studies of biomass burning. Although the N_2O/CO_2 molar ratios are in good agreement with results from other airborne studies, they are roughly a factor of 2 larger than N_2O/CO_2 molar ratios obtained from laboratory studies. While the possibility of some artifact production of N_2O in our canister samples cannot be completely discounted, it is unlikely that it could be responsible for the entire discrepancy between our results and those obtained from laboratory studies. A more likely explanation for the higher N_2O/CO_2 molar ratios obtained from our study (and other airborne studies of biomass burning) is the emission of N_2O from the soil, which is not accounted for in laboratory studies.

In addition to using our measurements to estimate the fluxes of various chemical species from temperate and boreal fires, we have outlined a new method for assessing the global fluxes of CH_4, NMHC, H_2 and NH_3 from biomass burning. This method uses the CO/CO_2 mass ratio as the independent variable in regression equations to predict emission factors for CH_4, NMHC, H_2 and NH_3 for the combustion of different biomass types. We have determined the annual global emissions of CH_4, NMHC, H_2 and NH_3 to be 8%, 17%, 24% and 7%, respectively, of the total global emissions of these four species. While these results show that biomass burning does not contribute the majority of global emissions of CH_4, NMHC, H_2 and NH_3, they nevertheless suggest that biomass burning is a significant contributor to the atmospheric reservoirs of these four species. Furthermore, given the seasonal nature of biomass burning, the percentage contributions of biomass burning to the global budgets of CH_4, NMHC, H_2 and NH_3 could be even higher during certain times of the year.

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